

PATENT SPECIFICATION

NO DRAWINGS

867.528



Date of Application and filing Complete Specification: Oct. 7, 1957.

No. 31283/57.

Four Applications made in United States of America on Oct. 12, 1956.

Complete Specification Published: May 10, 1961.

Index at acceptance:—Classes 2(3), C2B2(A2: D: F: G1A: G1B: G4: G6: G11: G12: J: K); and 2(6), P2A, P2D1(A: B), P2K7, P2P(1D: 1E1: 1E2: 1E5: 2B: 2C: 2X: 3: 5: 6A: 6C: 6H), P4A, P4D(1A: 2: 3A: 3B1: 3B3: 8), P4K7, P4P(1D: 1E1: 1E2: 1E5: 2B: 2C: 2X: 3: 5: 6A: 6C: 6H), P4T2G, P5A, P5D2(A: X), P5K7, P5P(1D: 1E1: 1E2: 1E5: 2B: 2C: 2X: 3: 5: 6A: 6C: 6H), P6A, P6D(1: 4), P6K7, P6P(1D: 1E1: 1E2: 1E5: 2B: 2C: 2X: 3: 5: 6A: 6C: 6H), P7A, P7D(1B: 2A1: 2A2A: 2A2B: 2A3: 2A4: 3: 8), P7K(2: 4: 5: 6: 7: 8: 9: 10: 11), P7P(1D: 1E1: 1E2: 1E5: 2B: 2C: 2X: 3: 5: 6A: 6C: 6H), P7T2(D: G), P8A, P8D(1A: 1B: 2A: 2B1: 2B2: 3A: 4: 5: 8), P8K7, P8P(1D: 1E1: 1E2: 1E5: 2B: 2C: 2X: 3: 5: 6A: 6C: 6H), P9A, P9D(1A1: 1B1: 1C: 3), P9K7, P9P(1D: 1E1: 1E2: 1E5: 2B: 2C: 2X: 3: 5: 6A: 6C: 6H), P10A, P10D(1A: 1X: 2A: 2X), P10K7, P10P(1D: 1E1: 1E2: 1E5: 2B: 2C: 2X: 3: 5: 6A: 6C: 6H), P11(A: D2A: K7), P11P(1D: 1E1: 1E2: 1E5: 2B: 2C: 2X: 3: 5: 6A: 6C: 6H).

International Classification:—C07c. C08f.

COMPLETE SPECIFICATION

Vinylphenyl Aminocarboxylic Compounds and Solid Resinous Polymers and Resinous Addition Polymers derived therefrom and methods of making same

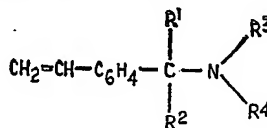
5 We, THE DOW CHEMICAL COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of City of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to novel vinylphenyl aminocarboxylic compounds. More particularly, it relates to novel aminocarboxylic acids having at least one amino group, at least one carboxyl group (at least one amino group and
15 at least one carboxyl group being attached to the same aliphatic carbon atom or adjacent aliphatic carbon atoms), and having at least one vinylphenyl radical as substituent on the aminocarboxylic acid nucleus; resinous polymers thereof; addition interpolymers comprising the product of polymeric combination of at least one vinylphenyl aliphatic aminocarboxylic acid compound and at least one other polymerizable ethylenically unsaturated compound;
20 and methods of preparing the foregoing compounds.

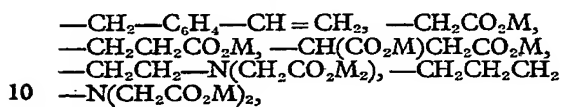
25 The products of this invention possess useful and advantageous properties as chelating and sequestering agents for metal ions. Although all of the products of this invention possess these common properties, they do not necessarily possess such properties to the same

degree. Individual products of this invention can readily be distinguished from other individual products and are particularly adapted to specific uses. They have application in some instances in solubilizing metals in compositions from which insoluble metal compounds would otherwise precipitate. In other instances they effect the precipitation of metals from compositions in which the metal would otherwise be soluble. Accordingly, these products are used to supply metals to compositions that are otherwise tolerant of such metals, and to inactivate or even to remove metal ions from compositions in which the presence of active metal ions is unwanted. The vinylphenyl aminocarboxylic products are unique in that they are also polymerizable and therefore have further advantage and utility in being capable of forming the polymeric materials of this invention also having chelating function. Therefore, the various products of this invention are advantageously employed in industry and commerce.

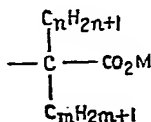
35 The present invention provides polymerizable vinylphenyl aminocarboxylic compounds having the general formula



wherein R^1 represents a hydrogen atom or a radical having the formula $-\text{CO}_2\text{M}$ or $-\text{CH}_2\text{CO}_2\text{M}$, R^2 represents a hydrogen atom or a methyl group, R^3 and R^4 are the same or different and each represent a hydrogen atom, a methyl group or a radical having the formula



or

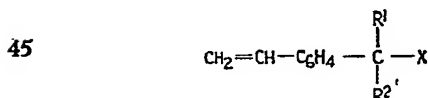


where M is a hydrogen atom, an ammonium radical or a metal, n is an integer from 1 to 4 inclusive and m is 0, 1 or 2, and wherein at least one of the radicals represented by R^1 , R^3 and R^4 contains a carboxyl group, and solid resinous polymers and resinous addition interpolymers of said polymerizable vinylphenyl aminocarboxylic compounds.

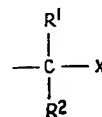
The invention also provides a solid resinous homopolymer of one polymerizable vinylphenyl aminocarboxylic compound as defined above and also a solid resinous copolymer of at least two or the said polymerizable vinylphenyl aminocarboxylic compounds as the only polymerically combined ingredients.

Furthermore, the invention provides a resinous addition interpolymer containing in polymerically combined form, an appreciable proportion of (A) at least one vinylphenyl aminocarboxylic compound as defined above and (B) at least a resinous addition interpolymer containing, in polymerically combined form, an appreciable proportion of (A) at least one vinylphenyl aminocarboxylic compound as claimed in claim 1 and (B) at least one polymerizable ethylenically unsaturated compound that is different from the compounds of (A).

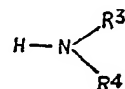
The present invention further provides a process for the preparation of a vinylphenyl aminocarboxylic compound or a polymer thereof as defined above, which comprises reacting a compound of the general formula:



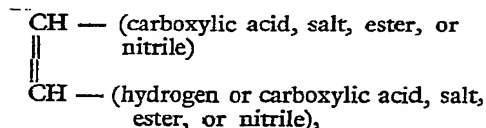
wherein R^1 represents a hydrogen atom or a radical having the formula $-\text{CO}_2\text{M}$, or $-\text{CH}_2\text{CO}_2\text{M}$, where M is as previously defined, R^2 represents a hydrogen atom or a methyl group and X represents a halogen atom or an amino radical having at least one amino hydrogen atom, or the whole group



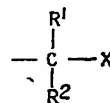
represents the formyl group, with (a) an aminocarboxylic acid, salt, ester, or nitrile having an $>\text{NH}$ or $-\text{NH}_2$ group when X is a halogen atom, said aminocarboxylic reactant having the general formula



wherein R^3 and R^4 correspond to the radicals previously defined and at least one of R^3 and R^4 contains a carboxylic acid, salt, ester, or nitrile group, (b) an ethylenically unsaturated carboxylic acid, salt, ester, or nitrile or halocarboxylic acid when X is an amino radical having at least one amino hydrogen atom, said ethylenically unsaturated carboxylic or nitrile reactant having the general formula



or (c) an alkali cyanide and ammonia when

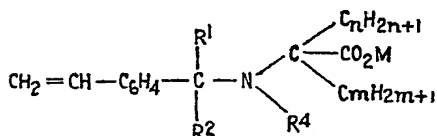
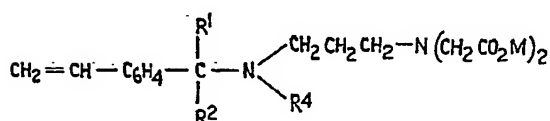
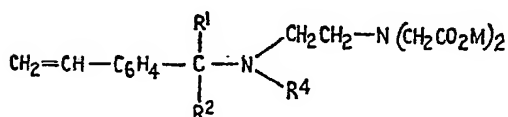
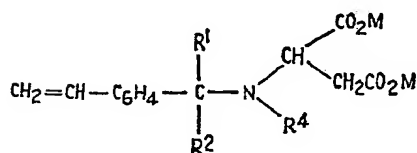
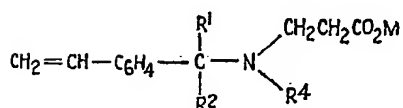
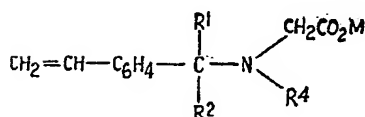
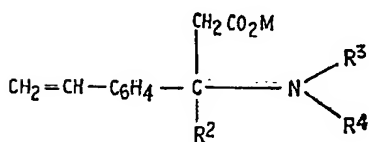
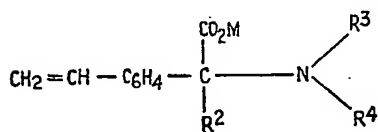


is the formyl group, and hydrolyzing the reaction product where necessary, to obtain said vinylphenyl aminocarboxylic compound, which may then be polymerised under free radical-inducing conditions.

The invention further provides a method of making a solid resinous polymer as defined above, which comprises subjecting at least one of the polymerizable vinylphenyl aminocarboxylic compounds of this invention to free radical-inducing conditions.

A still further provision of the invention is a method of making a resinous addition interpolymer which comprises subjecting to free radical-inducing conditions a polymerizable mixture comprising appreciable proportions of (A) at least one vinylphenyl aminocarboxylic acid compound having the formula set forth above and (B) at least one polymerizable ethylenically unsaturated compound that is different from the compounds of (A).

Within the vinylphenyl aminocarboxylic acids and salts having the general formula set forth above there are the following types of compounds.



wherein the symbols have the meanings previously given.

The following specific compounds are illustrative of these vinylphenyl substituted aminocarboxylic acids:

- 5 N,N-bis(ar-vinylbenzyl)glycine
- N-(ar-vinylbenzyl)sarcosine
- N-(ar-vinylbenzyl)alanine
- 10 N,N-bis(ar-vinylbenzyl)alanine
- N-(ar-vinylbenzyl)-β-alanine

- N,N-bis(ar-vinylbenzyl)-β-alanine
- N-(ar-vinylbenzyl)-2-aminobutyric acid
- N-(ar-vinylbenzyl)-2-aminoisobutyric acid
- N-(ar-vinylbenzyl)isovaline
- 15 N-(ar-vinylbenzyl)valine
- N-(ar-vinylbenzyl)norvaline
- N-(ar-vinylbenzyl)leucine
- N-(ar-vinylbenzyl)isoleucine
- N-(ar-vinylbenzyl)iminodiacetic acid
- 20 N-(ar-vinylbenzyl)-2-(vinylphenyl)glycine
- N-carboxymethyl-N-(ar-vinylbenzyl)aspartic acid
- 2-(vinylphenyl)iminodiacetic acid
- 2-(vinylphenyl)nitrilotriacetic acid
- 25 N-carboxymethyl-N-(ar-vinylbenzyl)alanine
- N-carboxymethyl-N-(ar-vinylbenzyl)-β-alanine
- N-carboxymethyl-N-(ar-vinylbenzyl)-2-aminobutyric acid
- 30 N-carboxymethyl-N-(ar-vinylbenzyl)-2-aminoisobutyric acid
- N-carboxymethyl-N-(ar-vinylbenzyl)isovaline
- N-carboxymethyl-N-(ar-vinylbenzyl)valine
- 35 N-carboxymethyl-N-(ar-vinylbenzyl)norvaline
- N-carboxymethyl-N-(ar-vinylbenzyl)leucine
- N-carboxymethyl-N-(ar-vinylbenzyl)isoleucine
- 40 N-(ar-vinylbenzyl)aspartic acid
- N,N-bis(ar-vinylbenzyl)aspartic acid
- N-(ar-vinylbenzyl)-3,3'-iminodipropionic acid
- 2-(vinylphenyl)glycine
- 45 3-(vinylphenyl)β-alanine
- 3-(vinylphenyl)-2-aminobutyric acid
- N-carboxymethyl-N-(ar-vinylbenzyl)-2-(vinylphenyl)glycine

These new vinylphenyl aminocarboxylic acid compounds may be prepared by reacting an aliphatic aminocarboxylic compound, i.e. an acid, salt, ester or nitrile, wherein the amino group has at least one hydrogen atom and is in one of the positions α- or β- relative to the carboxylic group, with an ar-vinylbenzyl halide in the presence of aqueous alkali.

The new vinylphenyl aminocarboxylic compounds may also be formed by reacting an ar-vinylbenzylamino compound having at least one amino hydrogen atom with an ethylenically unsaturated carboxylic acid, salt, ester or nitrile, e.g. diethyl maleate or acrylonitrile, and hydrolyzing the resulting reaction product.

Alternatively, the ar-vinylbenzylamino compounds may be reacted with monohalo-carboxylic acids such as a monohaloacetic acid in the presence of an aqueous alkali.

Furthermore, compounds, such as a 2-(ar-vinylphenyl)glycine, may be prepared by reacting an ar-vinylbenzaldehyde, an alkali cyanide, and ammonia in an alkaline aqueous reaction mixture.

The vinylphenyl aminocarboxylic compounds of this invention are characterized by the ability to polymerize. The individual vinyl-

phenyl aminocarboxylic acids can be polymerized to obtain homopolymers, and mixtures of the vinylphenyl aminocarboxylic acids can be polymerized under free radical-inducing conditions to obtain copolymers or interpolymers. The polymers of these vinylphenyl aminocarboxylic acids are capable of chelating metal ions in a manner analogous to that of the corresponding monomeric materials. Homopolymers of one of the above defined vinylphenyl aminocarboxylic compounds and copolymers of two or more of said compounds, are solid resinous materials which possess a unique combination of properties, i.e., the properties of resinous polymers, the properties of amphoteric ion exchange resins and the properties of chelation agents for certain metal ions.

Anion exchange resins containing active amino groups and cation exchange resins containing active carboxyl groups are, of course, already known. The new solid resinous homopolymers and copolymers of this invention are unique in that these products contain a plurality of groups having both amino and carboxyl groups at least one of each of which is attached to the same or adjacent carbon atoms, i.e. α -, or β -aminocarboxylic acid groups. Because of this particular combination of functional groups, the products of this invention form stable chelates with many polyvalent metal ions such as copper, mercury, cobalt, iron, nickel, manganese, lead, and the like. They do not form chelates with alkali metal ions. In most instances, they form weak chelates with alkaline earth metal ions, e.g. with magnesium, calcium, barium and strontium.

The complex chelates of these resins with chelate-forming metal ions differ from the reaction products of cation exchange resins and metal ions in that the cation exchange resin metal compositions are simple ionizable salts whereas the present resin chelates of metals are inherently molecular complexes possessing one or more coordinate covalent linkages. Since the chelate structure is much more stable than simple salt structures, the complexes of chelate-forming metals with the present chelating resins are much more stable than simple ion exchange resin salts. For this reason, the present chelating resins are particularly advantageous for use in removing chelate-forming metal ions from liquid compositions comprising the same, even in extremely dilute concentrations, in separating chelate-forming metal ions from non-chelate-forming metal ions, and in selectively separating chelate-forming metal ions from each other on the basis of different degrees of stability of the corresponding chelate complexes.

Resinous addition interpolymers may also be formed from the above defined vinylphenyl aminocarboxylic compounds, and contain, in polymerically combined form, appreciable

proportions of (A) at least one of said vinylphenyl aminocarboxylic compounds, and (B) at least one polymerizable ethylenically unsaturated compound that is different from the compounds of (A).

Any of the many known polymerizable ethylenically unsaturated compounds can be copolymerized with the vinylphenyl aminocarboxylic acid compounds to make the addition interpolymers of this invention. Among such known polymerizable ethylenically unsaturated compounds are the alkenyl-aromatic compounds, i.e. the styrene compounds, the ethylenically unsaturated acids and derivatives such as the acrylic acids and salts, acrylic esters, acrylic nitriles, acrylic amides, acrylic anhydrides, maleic esters, maleic anhydride, maleic acid polyesters, unsaturated alcohol esters, unsaturated ketones, unsaturated ethers, and other compounds containing one or more ethylenic linkages capable of addition polymerization. Specific examples of such ethylenically unsaturated compounds are styrene, α -methylstyrene, ar-methylstyrene, ar-ethylstyrene, α , ar-dimethylstyrene, ar, ar-dimethylstyrene, divinylbenzene, vinylnaphthalene, divinylbenzenesulfonic acid, divinylbenzenesulfonic acid, hydroxystyrene, methoxystyrene, aminostyrene, cyanostyrene, acetylstyrene, monochlorostyrene, dichlorostyrene and other halostyrenes, acrylic acid and salts, methacrylic acid and salts, methyl methacrylate, ethyl acrylate, glycol diacrylate, hexyl acrylate, phenyl acrylate, allyl acrylate, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, acrylanilide, acrylic anhydride, ethyl α -chloroacrylate, ethyl maleate, maleic anhydride, polyglycol maleate, diallyl fumarate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl benzoate, vinyl chloride, vinyl bromide, vinylidene chloride, vinylidene bromide, vinylidene cyanide, vinyl methyl ketone, isopropenyl ketone, vinyl carbazole, vinyl ethyl ether, divinyl ether, isobutylene, 1,3-butadiene and isoprene.

The addition of interpolymers of this invention comprising the monomeric starting materials in polymerically combined form, are in most instances hard, brittle, solid resins. The properties of these products very greatly depending upon the kind and proportion of starting materials that are polymerically combined. In polymers derived from starting mixtures containing only a small proportion of a vinylphenyl aminocarboxylic acid, the presence of the aminocarboxylic acid group makes the base polymer more hydrophilic and polar. Such groups in the polymer permit the introduction into the polymer structure of dyestuffs or of metal ions that can serve as mordants for dyes.

Polymers that contain at least 50 per cent by weight of one or more vinylphenyl α - or β -aminocarboxylic acid compounds polymerically combined are particularly useful for chelating metal ions. The resins that are insoluble in

water are advantageously employed to separate chelate-forming metal ions from solutions containing the same, even extremely dilute solutions, to separate chelate-forming metal ions from non-chelate-forming metal ions, and to separate chelate-forming metal ions from each other on the basis of the strength and stability of the respective chelate structures. Chelate-forming metal ions can be removed from their liquid solutions by stirring a quantity of one of these insoluble chelating resins in finely divided form into such ionic solutions, forming the metal chelate of the resin, and separating the metal-containing solid resin from the residual liquid, e.g. by filtration or decantation. Alternatively, the particulate solid resin can be dispersed as a permeable bed or layer, and the chelate-forming metal solution can be passed through such permeable bed or layer, whereby the chelate-forming metal ions react with and are retained by the solid resin in the bed. Since most of the metal chelates are less stable at low pH values, the metal-containing solid chelated resin can be regenerated by washing with strong acids, e.g. hydrochloric acid, whereby the metal ions are removed from the resin and can be separately recovered if desired.

The vinylphenyl α - and β -amino-carboxylic compounds of this invention can be polymerized in mass i.e., in the absence of diluents, or in solution, or in suspension in non-solvent media to obtain the resinous products of this invention, as illustrated by examples to follow. Homopolymers are obtained from individual polyphenyl α - or β -aminocarboxylic acids, and interpolymers are obtained by polymerization of mixtures of two or more of such polymerizable amino acids. Polymerization of these amino acids is initiated by free radical-inducing conditions and is accelerated by heat, by activation with ionizing radiations, and by contact with catalysts such as α , α' -azobisisobutyronitrile and the peroxygen compounds, e.g. persulphates and peroxides.

In most instances, the solid resinous polymers of the vinylphenyl aminocarboxylic acids are insoluble or only sparingly soluble in water. Some of the non-crosslinked polymers, e.g. of mono-vinyl monomers, are soluble in aqueous alkali. The cross-lined polymers, e.g. of polyvinyl monomers, are generally insoluble or only swellable with water or aqueous alkali.

The addition interpolymers of this invention are prepared by subjecting to free radical-inducing conditions a composition comprising an intimate mixture of an appreciable proportion of at least one of the polymerizable vinylphenyl α - or β -aminocarboxylic acid compounds and an appreciable proportion of at least one other polymerizable ethylenically unsaturated compound, both as hereinbefore identified. The proportions of the diverse kinds of polymerizable monomers in the mixture can, of course, be varied widely depending upon

the kind of copolymer product desired. Compositions predominating in one or more vinylphenyl amino-carboxylic acid compounds give rise to copolymers whose properties are predominately those of the polymerized vinylphenyl amino-carboxylic acid as advantageously modified in kind and degree by the other polymerizable ethylenically unsaturated compound chemically combined in the copolymer. Those compositions that predominate in such other polymerizable ethylenically unsaturated monomer give rise to copolymer products whose properties are predominately those of the polymerized ethylenically unsaturated monomer as advantageously modified in kind and degree by the vinylphenyl aminocarboxylic acid compound chemically combined therein. In some instances the amount of one of these kinds of materials required to significantly modify the polymer properties is extremely small. For instance, only a small amount, e.g. 0.5 per cent by weight, of divinylbenzene in a vinylphenyl aminocarboxylic acid provides a copolymer having an appreciable degree of cross-linking thereby decreasing its solubility and swellability by aqueous media. On the other hand, only a small amount, e.g. 0.5 per cent by weight, of a vinylphenyl aminocarboxylic acid in a hydrophobic ethylenically unsaturated monomer provides a co-polymer having an appreciable increase in hydrophilic properties. In most instances, the polymers of this invention are derived from starting mixtures containing from 1 to 99 parts by weight of each of the starting monomers.

The polymerization of the starting mixture of monomers can be carried out in mass, i.e. in the absence of any diluent, in solution in solubilizing liquids, or while suspended in non-solvent liquids. The polymerization is initiated by free radical-inducing conditions and is accelerated by heat and catalyzed by exposure to ionizing radiations and by contact with free radical catalysts such as α , α' -azobisisobutyronitrile and the peroxygen compounds such as cumene hydroperoxide and potassium persulphate.

The following examples illustrate the new vinylphenyl aminocarboxylic acids, certain of their characteristics, and suitable methods for their preparation.

EXAMPLE 1.

Preparation of N-(*ar*-vinylbenzyl)iminodiacetic acid.

Into a 5-litre round-bottom flask fitted with a mechanical stirrer, reflux condenser, and dropping funnel were placed 133 grams of iminodiacetic acid, 1 litre of water, 1.5 litres of methanol, and a solution of 66 grams of sodium hydroxide in 250 ml. of water. Stirring was begun, and the contents of the flask were heated to reflux. From the dropping funnel there were added to the reaction mixture 153 grams of *ar*-vinylbenzyl chloride over a period

of one hour. After approximately one-fourth of the ar-vinylbenzyl chloride had been added, another portion of 66 grams of sodium hydroxide in 250 ml. of water was added all at once to the reaction mixture, and the addition of ar-vinylbenzyl chloride was continued. Heating of the reaction mixture was discontinued after completion of the addition of the ar-vinylbenzyl chloride, but stirring was continued for a further 30 minutes.

The methanol was distilled from the reaction mixture, and the cooled aqueous residue was four times extracted with 25-ml. portions of chloroform. A small amount of decolorizing carbon was stirred into the aqueous solution and the mixture was filtered. The clear filtrate was heated to drive off traces of chloroform, and was cooled and acidified with monconcentrated hydrochloric acid to a pH value of 2.

The white solid crystalline precipitate that formed was collected on a filter and dried. The crystalline product consisted substantially of N-(ar-vinylbenzyl)iminodiacetic acid and sodium chloride. Recrystallization from water produced substantially pure N-(ar-vinylbenzyl)iminodiacetic acid having the analyses shown in Table I.

The acid dissociation constants of N-(ar-vinylbenzyl)iminodiacetic acid were determined by titration as follows: Sufficient solid amino acid was dispersed in 200 ml. of 1N potassium chloride solution to make the solution approximately $10^{-3}M$ in respect to the amino acid. The solution was then potentiometrically titrated with standardized 0.1N potassium hydroxide solution. From these titration data, the acid dissociation constants were calculated.

$$\begin{aligned}\text{First } H^+: k_1 &= 5.14 \times 10^{-3} \\ \text{Second } H^+: k_2 &= 2.40 \times 10^{-9}\end{aligned}$$

EXAMPLE 2.

Preparation of N,N-bis(ar-vinylbenzyl)glycine Run 1.

Into a 1-litre, 3-necked flask was charged 75.1 g. of glycine, 100 ml. of dioxane, and 300 ml. of water at 60° C. To the resulting mixture there were concurrently, separately, and slowly added 76.3 g. of ar-vinylbenzyl chloride and a solution of 77 ml. of 19.5 N sodium hydroxide solution in 75 ml. of water, the additions being made over a 45-minute period with continued stirring while the temperature of the reaction mixture was maintained at 70° C. The rate of addition of the sodium hydroxide solution was such as to maintain the pH value of the reaction mixture in the range from 8 to 10 during the course of the reaction.

After standing overnight at room temperature, the reaction mixture was extracted with chloroform. The chloroform extract was acidified with hydrochloric acid and diluted with water, whereupon a slurry of crystalline solid formed. The solid was collected on a

filter, was washed with water and dried.

Analysis of the recrystallized N,N-bis(ar-vinylbenzyl)glycine for ethylenic unsaturation using standardized bromate-bromide solution and glacial acid as titration medium, was as shown in Table I.

Run 2.

In a manner analogous to that just described in Run 1, 150 g. of glycine was reacted with 152.6 g. of ar-vinylbenzyl chloride in 800 ml. of water as reaction medium, adding strong sodium hydroxide solution during the course of the reaction to maintain the pH of the reaction mixture at values between 8 and 10. Upon standing at room temperature, the reaction mixture formed two layers. These layers were separated, and each was extracted with ether and separately neutralized with hydrochloric acid, forming a crystalline precipitate in each instance. The solids were separately collected, washed and dried. There were thereby obtained 61.5 g. and 54 g. of N,N-bis(ar-vinylbenzyl)glycine from the lower and upper layers, respectively, of the reaction mixture. After recrystallization from hot 95 per cent ethanol, the N,N-bis(ar-vinylbenzyl)glycine had the analyses shown in Table I.

The N,N-bis(ar-vinylbenzyl)glycine is not soluble per se in water. The amino acid was dissolved in an excess of alkali. Although the alkaline solution could be back-titrated with acid, rapid titration appeared to be a non-equilibrium process. An equilibrium titration was obtained by dissolving a test portion of the amino acid in a KCl solution containing an excess of standard KOH, adding a small amount of standard acid, closing the mixture in a container under an atmosphere of nitrogen free of carbon dioxide, tumbling the container at 30° C. until a steady pH value was obtained, adding a little more acid, and repeating the process until the titration curve was obtained. From these data, the dissociation constants for N,N-bis(ar-vinylbenzyl)glycine were found to be as follows:

$$\begin{aligned}k_1 &= 2.27 \times 10^{-2} \\ k_2 &= 1.67 \times 10^{-9}\end{aligned}$$

EXAMPLE 3.

Preparation of N-(ar-vinylbenzyl)isovaline.

A mixture of 200 ml. of water, 50 ml. of dioxane and 47 g. of isovaline, together with a trace of hydroquinone, was heated to a temperature in the range from 55° to 60° C. in a stirred reaction vessel fitted with reflux condenser and dropping funnels. Over a period of one hour, there were concurrently added to the reaction mixture 15.3 g. of ar-vinylbenzyl chloride and 31.2 g. of sodium hydroxide.

After an additional hour of stirring, the reaction mixture was diluted with an equal volume of water and then was extracted with chloroform. The extracted water solution was acidified with hydrochloric acid to a pH value of 5.5, whereupon a white solid precipitate

formed. The solid was collected, washed and dried to obtain 9.7 g. of N-(ar-vinylbenzyl)-isovaline having the analyses shown in Table I.

EXAMPLE 4.

Preparation of N-(ar-vinylbenzyl)-2-(p-vinylphenyl)glycine.

A mixture of 2 g. of 2-(p-vinylphenyl)-glycine (from Example 8), 50 ml. of water and 10 ml. of dioxane was heated to 70° C. A total of 1.7 g. of ar-vinylbenzyl chloride was added in two portions about 15 minutes apart while the reaction mixture was stirred and the temperature was maintained about 70° C. The pH value of the reaction mixture was maintained between 9 and 11 by adding 2 ml. of 50 per cent by weight sodium hydroxide solution dropwise as needed over a one-hour period. After 4.5 hours of heating and stirring, the reaction mixture was cooled and filtered. The filtrate was extracted with ether and the aqueous layer was acidified with hydrochloric acid to a pH value of about 5. A precipitated pale yellow solid was collected and washed with water. The solid was redissolved in dilute aqueous alkali and reprecipitated with hydrochloric acid. The reprecipitated N-(ar-vinylbenzyl)-2-(p-vinylphenyl)glycine was collected, washed and dried. The analyses of the N-(ar-vinylbenzyl)-2-(p-vinylphenyl)glycine are shown in Table I.

EXAMPLE 5.

In the foregoing Examples 1—4 a number of vinylphenyl aminocarboxylic acids were prepared by reaction of ar-vinylbenzyl chloride with aminocarboxylic acids having at least one hydrogen atom on the amino group. The ar-vinylbenzyl chloride employed in these Examples was a mixture of isomers consisting essentially of from 60 to 65 per cent by weight of *p*-vinylbenzyl chloride and from 40 to 35 per cent of *o*-vinylbenzyl chloride. In place of this particular isomeric mixture there can be used any of the individual isomers, i.e., *o*-vinylbenzyl chloride, *m*-vinylbenzyl chloride, or *p*-vinylbenzyl chloride, or mixture of two or more of such isomeric ar-vinylbenzyl chlorides to obtain the corresponding *o*-, *m*-, or *p*-vinylphenyl-substituted amino carboxylic acid or mixture thereof. In place of ar-vinylbenzyl chloride there can be used an ar-vinylbenzyl bromide with substantially the same results. In a manner analogous to that shown in Examples 1—4, the following vinylphenyl aminocarboxylic acids can be prepared by reaction in an alkaline aqueous medium of ar-vinylbenzyl chloride or ar-vinylbenzyl bromide and the amino acids as follows:

N-(ar-vinylbenzyl)sarcosine; from sarcosine;
N-(ar-vinylbenzyl)alanine; from alanine;
N,N - bis(ar - vinylbenzyl)alanine, from alanine;
N - (ar - vinylbenzyl) - β - alanine, from β -alanine;
N,N-bis(ar-vinylbenzyl)- β -alanine, from β -

alanine;

N-(ar-vinylbenzyl)-2-aminobutyric acid from 2-aminobutyric acid;

N-(ar-vinylbenzyl)-2-aminoisobutyric acid from 2-aminoisobutyric acid;

N-(ar-vinylbenzyl)valine, from valine;

N-(ar-vinylbenzyl)norvaline, from norvaline;

N-(ar-vinylbenzyl)leucine, from leucine; and

N-(ar-vinylbenzyl)isoleucine, from isoleucine.

In carrying out these reactions, the amino acid and the ar-vinylbenzyl halide are dispersed in an aqueous medium that may also contain a further solubilizing agent such as dioxane or an alcohol. Sufficient alkali is added to the dispersion to maintain a neutral to alkaline reaction mixture, i.e. a pH value of at least 7, preferably in the range from 8 to 11. Suitable alkalis are the alkali metal hydroxides and carbonates such as sodium hydroxide, potassium hydroxide, sodium carbonate, and potassium carbonate. The reaction is accelerated by heating the reaction mixture and can conveniently be carried out at temperatures from room temperature to the boiling point of the reaction mixture. The amino acid product is usually obtained from the resulting reaction mixture by adjusting the pH value of the mixture to the isoelectric point by the amino acid, e.g. by addition to the aqueous reaction mixture of a strong acid such as hydrochloric acid, and collecting the precipitated aminocarboxylic acid.

EXAMPLE 6.

Preparation of N-(ar-vinylbenzyl)aspartic acid.

A solution of 34 g. of ar-vinylbenzylamine hydrochloride in 200 ml. of water was made alkaline by addition thereto of a solution of 9.6 g. of sodium hydroxide in 80 ml. of water. The liberated ar-vinylbenzylamine was extracted from the aqueous mixture with one 60-ml. and two 40 ml. portions of ether. After drying over anhydrous Na₂SO₄, the combined ether solutions were added to 68.8 g. of diethyl maleate. The resulting mixture was allowed to stand at room temperature for six days, after which 200 ml. of water and 16 ml. of concentrated hydrochloric acid were added with agitation. The ethereal layer was withdrawn and the aqueous layer was extracted with 20 ml. of ether. The aqueous layer was made strongly basic with 50 per cent by weight sodium hydroxide, thereby precipitating an oil. The oil was extracted from the aqueous solution with two 20-ml. portions of ether. The ether extract was dried over anhydrous Na₂SO₄. Evaporation of the ether produced 49.1 g. of crude diethyl N-(ar-vinylbenzyl)-aspartate, $n_D^{24} = 1.5144$. Other analyses are recorded in Table I, from which it can be deduced that the crude ester contained a small amount of polymer.

A mixture of 49.1 g. of the crude ester, 16.1 g. NaOH, and 150 ml. of water was heated under reflux for approximately three hours until the oily layer disappeared. The

hydrolysis mixture was acidified to a pH value of approximately 2 by addition thereto of hydrochloric acid. The solid precipitate was collected, washed, and recrystallized from 70 ml. of boiling water. The recrystallized product was collected, washed and dried to obtain 30 g. of N-(ar-vinylbenzyl)aspartic acid which still contained some occluded sodium chloride. Analyses of the product are shown in Table I. From the titration of N-(ar-vinylbenzyl)aspartic acid at 10^{-3} M. concentration in N/1 KCl solution with N/10 KOH solution, at 30° C., the acid dissociation constants were calculated as follows:

$$K_a = 1.78 \times 10^{-9}$$

$$K_b = 1.78 \times 10^{-9}$$

The ar-vinylbenzylamine employed in this Example 6 was a mixture of isomeric ar-vinylbenzylamines consisting essentially of from 60 to 65 per cent by weight of *p*-vinylbenzylamine and from 40 to 35 per cent of *o*-vinylbenzylamine. In place of this particular mixture of isomers, there can be used any of the individual isomers, i.e. *o*-vinylbenzylamine, *m*-vinylbenzylamine, *p*-vinylbenzylamine, or mixture of two or more of these isomeric ar-vinylbenzylamines, to obtain the corresponding *o*-, *m*-, or *p*-vinylbenzyl-substituted aminocarboxylic acid or mixture thereof.

EXAMPLE 7.

The preparation of N-(ar-vinylbenzyl)aspartic acid in Example 6 is representative of the preparation of a vinylphenyl aliphatic aminocarboxylic acid by reaction of an ar-vinylbenzylamine and an activated ethylenically unsaturated carboxylic acid-forming progenitor. In a similar manner, N,N-bis(ar-vinylbenzyl)amine can be reacted with diethyl maleate to form diethyl N,N-bis(ar-vinylbenzyl)aspartate, which can then be hydrolyzed to produce N,N-bis(ar-vinylbenzyl)aspartic acid.

Ar-vinylbenzylamine also adds to the ethylenic linkage of acrylonitrile. Accordingly, ar-vinylbenzylamine can be reacted with one mole of acrylonitrile to form 3-(ar-vinylbenzylamino)propionitrile which is then hydrolyzed to N-(ar-vinylbenzyl)- β -alanine. The addition of two moles of acrylonitrile to ar-vinylbenzylamine produces N-(ar-vinylbenzyl)-3,3'-iminodipropionitrile which is then hydrolyzed to N-(ar-vinylbenzyl)-3,3'-iminodipropionic acid. Similarly, the addition of N,N-bis(ar-vinylbenzyl)amine to acrylonitrile and hydrolysis of the 3-(N,N-bis(ar-vinylbenzyl)amino)propionitrile produces N,N-bis(ar-vinylbenzyl)- β -alanine.

EXAMPLE 8.

Preparation of 2-(*p*-vinylphenyl)glycine.

A solution of 132 g. of *p*-vinylbenzaldehyde in 250 ml. of methanol was added to a solution of 53.5 g. of ammonium chloride and 51.0 g. of sodium cyanide in 100 ml. of concentrated ammonium hydroxide and 200 ml. of water. To the reaction mixture was added

approximately one gram of tert-butylcatechol and the reaction mixture was heated with intermittent stirring at approximately 50° C. for one hour. The resulting reaction mixture was diluted with an equal volume of water, and treated with a solution of 160 g. of sodium hydroxide in one liter of water and 250 ml. of methanol.

The resulting mixture was heated at reflux for one hour, cooled, and extracted with 200 ml. of benzene. The benzene extract was in turn extracted with a small amount of 1 N sodium hydroxide solution. The sodium hydroxide extract was combined with the main aqueous reaction mixture and the combined mixture was acidified with dilute hydrochloric acid to a pH value of approximately 6. The yellow solid precipitate was collected, washed with water, and redissolved in dilute hydrochloric acid. After treatment with decolorizing carbon and filtration through filter aid, the clear acid solution was partially neutralized with sodium hydroxide solution to a pH value of approximately 6. The precipitated solid was collected, washed and dried to provide 37.9 g. of 2-(*p*-vinylphenyl)glycine, the analyses of which were as shown in Table I.

2-(Vinylphenyl)glycine can also be made by reacting vinylbenzaldehyde with sodium cyanide and ammonium bicarbonate to form 5-(vinylphenyl)hydantoin, and hydrolyzing the latter.

EXAMPLE 9.

Preparation of 3-(*p*-vinylphenyl)- β -alanine.

To a solution of 12.6 g. of malonic acid in 6 g. of concentrated ammonium hydroxide were added 13.2 g. of *p*-vinylbenzaldehyde and 50 ml. of absolute alcohol. The resulting mixture was heated on a steam bath until the alcohol was evaporated and evolution of carbon dioxide ceased. The residue was dispersed in 200 ml. of water and an excess of hydrochloric acid was added to produce a granular precipitate that was collected. The filtrate was evaporated and extracted with ether. Evaporation of the ether produced a further quantity of solid product. Further concentration of the aqueous liquor gave another crop of solid product. The total yield of crude 3-(*p*-vinylphenyl)- β -alanine was approximately 10 g. The product was recrystallized from hot water. Analyses of the recrystallized product were shown in Table I.

In place of the *p*-vinylbenzaldehyde employed in the foregoing Examples 8 and 9, there can be employed another of the isomeric ar-vinylbenzaldehydes, i.e., *m*-vinylbenzaldehyde or *o*-vinylbenzaldehyde, or mixtures of two or more of such ar-vinylbenzaldehydes to obtain the corresponding *o*-, or *m*-vinylphenyl-substituted amino carboxylic acid, or substituted amino carboxylic acid, or mixture of ar-vinylphenyl-substituted amino carboxylic acids.

The condensation of malonic acid and ammonia with acetylstyrene can also be carried out to produce 3-(vinylphenyl)-3-aminobutyric acid.

5 EXAMPLE 10.

Preparation of N-carboxymethyl-N-(ar-vinylbenzyl)aspartic acid.

A mixture of 12.5 g. N-(ar-vinylbenzyl)-aspartic acid (from Example 6), 7.1 g. of chloroacetic acid, and 85 ml. of water was placed in a 250 ml. reaction flask. The mixture was made alkaline to a pH value of approximately 10 by addition thereto of 50 per cent by weight aqueous sodium hydroxide, and the resulting mixture was heated to reflux for a period of 26 hours. During this time, concentrated aqueous sodium hydroxide solution was added as needed to maintain the pH value of the reaction mixture at approximately 10. When titration of a test sample for ionic chloride indicated substantially complete conversion of the chloroacetic acid, the reaction mixture was made strongly acidic (pH value of 2) with concentrated hydrochloric acid. N-Carboxymethyl-N-(ar-vinylbenzyl)aspartic acid separated as a heavy grease from the aqueous salt solution and was converted to a solid product by trituration with acetone. Analyses of the N-carboxymethyl-N-(ar-vinylbenzyl)-aspartic acid are shown in Table I. The ionization constants for the tribasic carboxylic acid were determined by potentiometric titration with 0.1N KOH of a 10^{-3} M solution of the amino acid in 200 ml. of 1N KCl solution as follows:

$$\begin{aligned}k_1 &= 5.2 \times 10^{-3} \\k_2 &= 1.17 \times 10^{-5} \\k_3 &= 8 \times 10^{-10}\end{aligned}$$

40 EXAMPLE 11.

Preparation of 2-(p-vinylphenyl)iminodiacetic acid and 2-(p-vinylphenyl)nitrilotriacetic acid.

To a mixture of 3 g. of 2-(p-vinylphenyl)-glycine (from Example 8) 3 g. of sodium carbonate and 25 ml. of water, were added a solution of 4.5 g. of sodium chloroacetate in 10 ml. of water and a trace of hydroquinone. The resulting mixture was heated at temperatures in the range from 70° to 80° C. for 8 hours, during which another 3 g. of sodium carbonate was added to the reaction mixture. After filtering the reaction mixture, the filtrate was acidified to a pH value of 2.5 with hydrochloric acid and was concentrated by evaporation in an air stream. The solid precipitate was collected, washed and dried. This product was a mixture of 2-(p-vinylphenyl)iminodiacetic acid (condensation product of one molecular proportion of chloroacetic acid) and 2-(p-vinylphenyl)nitrilotriacetic acid (condensation product of two molecular proportions of chloroacetic acid). Recrystallization from hot water caused the separation of the mixture

into two fractions, the last soluble product being substantially the 2-(p-vinylphenyl)iminodiacetic acid. The more soluble product was substantially the 2-(p-vinylphenyl)nitrilotriacetic acid. Analyses are shown in Table I.

EXAMPLE 12.

Preparation of N-(ar-vinylbenzyl)iminodiacetic acid.

To a solution containing 1.9 g. of chloroacetic acid, 1.6 g. of sodium hydroxide, 20 ml. of water and a trace of hydroquinone was added 1.7 g. of ar-vinylbenzylamine hydrochloride. The reaction mixture was heated for 30 minutes on a steam bath, treated with decolorizing charcoal and filtered. The filtrate was acidified to a pH value of 1.8 by addition thereto of hydrochloric acid, forming a white precipitate. After concentration to about 15 ml. by blowing with air, the slurry was filtered, and the white crystals of N-(ar-vinylbenzyl)-iminodiacetic acid was washed with water and dried.

EXAMPLE 13.

Examples 10-12 are concerned with the preparation of N-carboxymethyl amino compounds by reactions involving chloroacetic acid. In similar manner, these and other amino acids can be made by reacting in an alkaline aqueous medium chloroacetic acid or bromoacetic acid and starting amino compounds that contain a vinylphenyl group and at least one hydrogen atom on the amino group, for example:

N-carboxymethyl-N-(ar-vinylbenzyl)alanine, from N-(ar-vinylbenzyl)alanine (Example 5);

N-carboxymethyl-N-(ar-vinylbenzyl)-β-alanine, from N-(ar-vinylbenzyl)-β-alanine (Example 5);

N-carboxymethyl-N-(ar-vinylbenzyl)-2-aminobutyric acid, from N-(ar-vinylbenzyl)-2-aminobutyric acid (Example 5);

N-carboxymethyl-N-(ar-vinylbenzyl)-2-aminoisobutyric acid, from N-(ar-vinylbenzyl)-2-aminoisobutyric acid, (Example 5);

N-carboxymethyl-N-(ar-vinylbenzyl)isovaline, from N-(ar-vinylbenzyl)isovaline (Example 5);

N-carboxymethyl-N-(ar-vinylbenzyl)valine, from N-(ar-vinylbenzyl)valine (Example 5);

N-carboxymethyl-N-(ar-vinylbenzyl)norvaline, from N-(ar-vinylbenzyl)norvaline (Example 5);

N-carboxymethyl-N-(ar-vinylbenzyl)leucine, from N-(ar-vinylbenzyl)leucine (Example 5);

N-carboxymethyl-N-(ar-vinylbenzyl)isoleucine, from N-(ar-vinylbenzyl)isoleucine (Example 5);

- N - carboxymethyl - N - (ar-vinylbenzyl)-2-(vinylphenyl)glycine, from N-(ar-vinylbenzyl)-2-(vinylphenyl)glycine (Example 4);
- 5 and N,N-bis(ar-vinylbenzyl)glycine, from bis-(ar-vinylbenzyl)amine.
- In carrying out these reactions, the vinylphenyl compounds that contain a —NH— group and the haloacetic acid are dispersed in an aqueous medium. Sufficient alkali is added to the dispersion to maintain a neutral to alkaline reaction mixture, i.e. a pH value of at least 7, preferably in the range from 8 to 11. Suitable alkalies are the alkali metal hydroxides and carbonates such as sodium hydroxide, potassium hydroxide, sodium carbonate, and potassium carbonate. The reaction is accelerated by heating the reaction mixture and can conveniently be carried out at temperatures from room temperature to the boiling point of the reaction mixture. The amino acid product is usually obtained from the resulting reaction mixture by adjusting the pH value of the mixture to the isoelectric point of the amino acid, e.g. by addition to the aqueous reaction mixture of a strong acid such as hydrochloric acid, and collecting the precipitated amino-carboxylic acid.
- The vinylphenyl aminocarboxylic acids illustrated by Examples 1—13 are in most instances solid, usually crystalline, products. In most instances they do not have sharp melting points but undergo decomposition when heated to elevated temperatures. They form salts of the carboxylic acid group by reaction with bases such as the ammonium bases, e.g. those formed by ammonia and organic amines, and with metal bases such as alkali metal and alkaline earth metal bases. Some of the metal base salts have chelate structures as shown in the succeeding example. These amino acids also form acid salts of the amino group, e.g. hydrochloride salts, at low pH values.
- 25
- 30
- 35
- 40

TABLE I

Example	Sample Compound	Nitrogen, Weight Percent		Neutral Equivalent*		Ethylenic Unsaturation**	
		Found	Calculated	Found	Calculated	Found	Calculated
1	N-(ar-vinylbenzyl) imino diacetic acid	5.36	5.62	3.86	4.01	3.64	4.01
2	N,N-bis(ar-vinylbenzyl)glycine, Run 1		4.56		3.26	6.31	6.52
	N,N-bis(ar-vinylbenzyl)glycine, Run 2	4.33	4.56	3.38	3.26	6.28	6.52
3	N-(ar-vinylbenzyl)isovaline	5.87	6.39		4.57	4.51	4.57
4	N-(ar-vinylbenzyl)-2-(p-vinylphenyl) glycine		4.77	3.3	3.4	6.3	6.8
6	Diethyl N-(ar-vinylbenzyl)aspartate	4.73	4.6	3.08	3.28	2.89	3.28
	N-(ar-vinylbenzyl)aspartic acid		5.61	3.66	4.01	3.62	4.01
8	2-(p-Vinylphenyl)glycine	7.43	7.90	5.48	5.64	5.50	5.64
9	3-(p-Vinylphenyl) β -alanine	7.56	7.33	5.24	5.24		5.24
10	N-carboxymethyl-N-(ar-vinylbenzyl)-aspartic acid		4.55	2.85	3.26		3.26
11	2-(p-Vinylphenyl)iminodiacetic acid	5.06	5.95	3.6	4.25	3.59	4.25
	2-(p-Vinylphenyl)nitrolotriacetic acid	4.89	4.78	3.59	3.41	3.54	3.41

* Milliequivalents per gram of sample, standard acid-alkali titre, based on the amino group in the amino acid.

** Milliequivalents per gram of sample, bromate-bromide titre, using glacial acetic acid solvent.

EXAMPLE 14

5 The vinylphenyl amino-carboxylic acids illustrated by the foregoing Examples are characterized by the ability to chelate metal ions in solution. Therefore, these compounds are useful chelation agents. Some representative examples of these chelates were prepared and their properties are shown in Table II. In most instances, the metal chelates were prepared by dispersing the amino acid compound in water or in 1N KCl solution, adding the metal ion in the form of its chloride salt, e.g. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and titrating the resulting dispersion with alkali such as KOH solution. In some instances, the metal ions formed chelate structures with the amino acids at low pH values.

In Table II, and elsewhere throughout the Examples, the chelate ratios are expressed in terms of the number of moles of amino acid ligand per atom of metal in the chelate complex. Studies of the chelates and determination of their Stability Constants were carried out substantially in accordance with the techniques described by Chaberek and Martell, J. Am. Chem. Soc. 74, 5052 (1952) and by J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," pp. 2—38, published by P. Haase and Son, Copenhagen (1941).

In most instances the metal chelates are stable at neutral to alkaline pH values. At low pH values, most of the metal chelates are dissociated.

TABLE II

Vinylphenyl Aliphatic Aminocarboxylic Acid	Metal Ion	Chelate	Chelate Stability Constants			Notes
			K_1	K_2	K_3	
N-(ar-vinylbenzyl)iminodiacetic acid	Cu ⁺²	1:1 & 2:1	3.48×10^{10}	7.94×10^4	—	1, 2
"	Co ⁺²	1:1 & 2:1	6.38×10^6	5.13×10^6	—	3, 6
"	Ni ⁺²	1:1 & 2:1	2.74×10^7	1.55×10^6	—	2, 4
"	Fe ⁺³	1:1 & 2:1 & 3:1	2.82×10^8	1.18×10^8	4.16×10^5	2, 4, 5
"	Fe ⁺²	1:1 & 2:1	2.94×10^5	3.8×10^4	—	10
"	Pb ⁺²	1:1 & 2:1	9.12×10^5	2.34×10^3	—	6
"	Mn ⁺²	1:1	2.25×10^6	—	—	4, 6
"	Mg ⁺²					7, 12
"	Ca ⁺²					
"	Ba ⁺²					
"	Sr ⁺²					
N,N-bis(ar-vinylbenzyl)glycine	Cu ⁺²	1:1	3.14×10^6	—	—	6, 11
N-(ar-vinylbenzyl)-2-(p-vinylphenyl)glycine	Cu ⁺²	2:1				7
N-(ar-vinylbenzyl)aspartic acid	Cu ⁺²	1:1 & 2:1	4.85×10^7	2.35×10^6	—	1, 2
N-carboxymethyl-N-(ar-vinylbenzyl) aspartic acid	Cu ⁺²	1:1 & 2:1	6.73×10^{11}	1.06×10^{10}	—	1, 2
3-(p-vinylphenyl)- β -alanine	Cu ⁺²	1:1 & 2:1				7, 8
2-(p-vinylphenyl)nitritotriacetic acid	Cu ⁺²	1:1 & 2:1				1, 2, 7, 9
2-(p-vinylphenyl)glycine	Cu ⁺²	1:1 & 2:1				7, 8

(notes to Table II)

- Note 1: Chelates soluble at pH all values.
- Note 2: 1:1 Chelate formed at low pH values.
- Note 3: 1:1 Chelate hydrolyzes at high pH values, but 2:1 chelate is soluble even at pH values over 10.
- Note 4: Chelates hydrolyze at high pH values.
- Note 5: Chelates precipitate at pH values between 5 and 8.
- Note 6: Chelates do not form at low pH with free acid but form with salts of the acid, e.g. the alkali metal salts.
- Note 7: Chelate Stability Constant not determined.
- Note 8: 2:1 Chelate not soluble above pH 4.
- Note 9: At high pH values each molecule of the salt form of the acid is capable of chelating more than 1 metal ion.
- Note 10: Chelates soluble at pH values below 9.5.
- Note 11: Free acid, salts and chelates are not sparingly soluble in water.
- Note 12: Chelates formed from N-(ar-vinylbenzyl)iminodiacetic acid and alkaline earth metals were weak and the Stability Constants were not calculated.

When a solution containing N-(ar-vinylbenzyl)iminodiacetic acid and a cupric salt in which the molar concentration of the amino acid is greater than the molar concentration of the cupric salt is titrated with standardized alkali solution, there are observed two inflection points in the titration curve, i.e., a plot of pH value of the sample against the amount of added alkali. One of these inflection points occurs at a pH value of approximately 5 and corresponds to the neutralization of two protons liberated from the 1:1 chelate complex of the amino acid and cupric ion, plus one proton from the normal dissociation of one of the carboxyl groups of the non-complexed excess amino acid at low pH. The excess, non-complexed portion of the amino acid, after neutralization of one of its carboxyl groups, dissociates at its second carboxyl group, thereby liberating another proton, the neutralization of which corresponds to the second inflection point at a pH value of approximately 8.5. The difference in the amount of standard alkali which is used between the first and second "end points" (i.e. inflection points on the titration plot) is a measure of the amount of the amino acid that is in excess over the amount of cupric copper in the solution. If the total amount of amino acid initially present in the titration sample is precisely known, the titre by difference is a quantitative measure of the amount of cupric

copper that is present, provided there are no other chelating metal ions also present.

The insoluble chelate of copper obtained with 3-(*p*-vinylphenyl)- β -alanine at an alkaline pH was analyzed;

Nitrogen, found, 5.81 per cent by weight

Nitrogen, calculated for

$(\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{CH}(\text{NH}_2)\text{CH}_2\text{CO}_2)_2-\text{Cu}\cdot 2\text{H}_2\text{O}$, 5.85 per cent by weight.

At alkaline pH values, an insoluble blue chelate of cupric copper was also obtained with 2-(*p*-vinylphenyl)glycine and was found to contain 6.28 per cent by weight nitrogen.

Nitrogen, calculated for

$(\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{CH}(\text{NH}_2)\text{CO}_2)_2-\text{Cu}\cdot 2\text{H}_2\text{O}$, 6.20 per cent by weight.

The following additional Examples illustrate the preparation, properties and uses of some of the resinous polymers of these vinylphenyl aliphatic amonicarboxylic acids, but the Examples are not to be construed as limiting the invention.

EXAMPLE 15.

Homopolymer of N-(ar-vinylbenzyl)iminodiacetic acid.

A solution of 23 grams of N-(ar-vinylbenzyl)iminodiacetic acid in 1300 mls. of water at a temperature of 90°C. was irradiated with ultraviolet radiation for three days. A pale yellow, fine powder, insoluble solid was separated from the solution in amount of approximately 11 grams. A further amount of solid

was obtained by concentration and irradiation of the residual aqueous solution.

The insoluble solid was a homopolymer of N-(ar-vinylbenzyl)iminodiacetic acid. Potentiometric titrations of the polymer were carried out in closed titration cells, with agitation and under an atmosphere of nitrogen free of carbon dioxide, the pH of the sample being measured by means of a glass calomel electrode system. The titrations were carried out by adding acid or base solutions in small increments and allowing equilibrium to be attained in each instance before adding the next increment of reagent.

From data obtained by so titrating a sample of polymeric N-(ar-vinylbenzyl)iminodiacetic acid, dispersed to a concentration of 1.831×10^{-3} molar in a 1N KCl solution, at 30°C., with standardized 0.1 N KOH solution, the acid dissociation constants for the polymer were calculated on the assumption of a homogeneous, single phase system, and were found to be as follows:

$$K_1 = 4.24 \times 10^{-4}$$

$$K_2 = 5.58 \times 10^{-10}$$

These values are somewhat lower than the corresponding values for the monomeric material.

Addition of cupric ions, e.g. as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, to a water dispersion of the polymeric N-(ar-vinylbenzyl)iminodiacetic acid caused the resin to turn blue, while the water phase remained colorless.

From a titration of the resin in the presence of cupric ions in the manner described above in this Example, the polymeric N-(ar-vinylbenzyl)iminodiacetic acid was found to form both 1:1 and 2:1 chelates (moles of resin: metal ion) with cupric ions, having Chelate Stability Constants, calculated on the assumption of a homogeneous, single phase system, as follows:

$$K_1 = 5.62 \times 10^9$$

$$K_2 = 1.38 \times 10^6$$

Addition of ferric ions, e.g. as FeCl_3 , to the water dispersion of the polymeric N-(ar-vinylbenzyl)iminodiacetic acid caused formation of a 1:1 chelate. Upon addition of alkali, 2:1 and 3:1 chelates (moles of resin-ferric ion) were formed, hydrolysis occurring above a pH value of 8.5. The Stability Constants for these chelates were found to be as follows:

$$K_1 = 1.20 \times 10^{10}$$

$$K_2 = 4.46 \times 10^7$$

$$K_3 = 7.94 \times 10^4$$

Polymeric N-(ar-vinylbenzyl)iminodiacetic acid forms stable chelates with iron and was used to remove iron ions from water solution, either by stirring the resin into, and filtering the resin chelate from, iron-containing aqueous solutions, or by passing such iron-containing liquids through a layer of the resin.

EXAMPLE 16.

Homopolymer of N,N-bis(ar-vinylbenzyl)-glycine.

A mixture of 17.8 g. of N,N-bis(ar-vinylbenzyl)glycine and 50 ml. of 1N NaOH, solution was heated to reflux and 14.4 mg. of sodium persulphate was added. After two hours, another 14.4 mg. of sodium persulfate was added and refluxing was continued. After 18 hours, 100 mg. of sodium persulfate and 150 ml. of water were added. After 48 hours the gelled product was diluted with one litre of water. Water was separated from the gel, and the gel was dispersed in one litre of dilute sodium hydroxide. The dispersion was heated, and filtered; the gel was thoroughly washed with water and dried under vacuum to obtain 16.5 g. of brittle yellow resinous polymer of N,N-bis(ar-vinylbenzyl)glycine.

Acid-base titrations of 0.1018 g. of the polymer dispersed in 200 ml. of 1N KCl solution were carried out under a CO_2 -free nitrogen atmosphere using the equilibrium method of incremental addition of reagents as described in Example 15. Similar titrations after addition of 0.0282 g. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ showed that the polymer formed 1:1 and 2:1 chelates with copper, the Stability Constants being as follows:

$$K_1 = 2.22 \times 10^5$$

$$K_2 = 4.20 \times 10^4$$

EXAMPLE 17.

Copolymer of N-(ar-vinylbenzyl)iminodiacetic acid and N,N-bis(ar-vinylbenzyl)glycine.

A solution containing 0.68 g. of N,N-bis(ar-vinylbenzyl)glycine, 16.2 g. of N-(ar-vinylbenzyl)iminodiacetic acid, 50 ml. of 1N KOH, and 300 ml. of water was heated to reflux. Sodium persulphate was added in several small portions over a period of about 8 hours to a total of 1.33 g. sodium persulphate. Acidification of the reaction mixture produced 13.35 g. of resinous copolymer of N-(ar-vinylbenzyl)iminodiacetic acid and N,N-bis(ar-vinylbenzyl)glycine.

EXAMPLE 18.

Homopolymer of 2-(p-vinylphenyl)glycine

A solution of 2 g. of 2-(p-vinylphenyl)glycine and 0.01 g. of sodium persulphate in 20 ml. of 1N NaOH was heated to incipient reflux. After 72 hours, 0.02 g. of sodium persulphate was added. After another 120 hours at incipient reflux, 0.05 g. of α, α' -azobisisobutyronitrile was added. Twenty four hours later, 0.05 g. of α, α' -azobisisobutyronitrile was added. After a total reaction time of 168 hours, the reaction mixture was cooled, acidified to a pH value of approximately 5 by addition thereto of dilute hydrochloric acid, and was filtered. The precipitated solid was washed with water and dried, whereby there was obtained polymerized 2-(p-vinylphenyl)glycine.

EXAMPLE 19.

Homopolymer of N-(ar-vinylbenzyl)aspartic acid.

- 5 A solution of 0.25 g. of N-(ar-vinylbenzyl)-
aspartic acid and 0.003 g. of sodium persul-
fate in 25 ml. of water was heated to reflux.
After 23 hours, 0.003 g. of sodium persulphate
was added, and reflux was continued for 27
10 hours to obtain 0.18 g. of tan-colored, resinous
polymerized N-(ar-vinylbenzyl)aspartic acid.

EXAMPLE 20.

Homopolymer of N-(ar-vinylbenzyl)-2-(p-
vinylphenyl)glycine.

- 15 An alkaline (sodium hydroxide) solution of
10 per cent by weight N-(ar-vinylbenzyl)-2-(p-
vinylphenyl)glycine and 0.2 per cent by weight
 α,α' -azobisisobutyronitrile was heated at 70°C.
for four days to obtain a gel which was
dialyzed against water. The dialyzed gel was
20 collected and dried to obtain a cross-linked
homopolymer of N-(ar-vinylbenzyl)-2-(p-
vinylphenyl)glycine.

EXAMPLE 21.

Homopolymer of N-(ar-vinylbenzyl)isovaline.

- 25 An alkaline (sodium hydroxide) solution of
N-(ar-vinylbenzyl)isovaline (10 per cent by
weight) and α,α' -azobisisobutyronitrile (0.2 per
cent by weight) was heated at 70°C. for four
30 days to obtain polymerized N-(ar-vinylbenzyl)-
isovaline.

EXAMPLE 22.

Homopolymer of 2-(p-vinylphenyl)nitritotri-
acetic acid.

- 35 An alkaline (sodium hydroxide) solution of
2-(p-vinylphenyl)nitritotriacetic acid, sodium
salt, (20 per cent by weight) and α,α' -azobis-
isobutyronitrile (0.2 per cent by weight) was
heated at 70°C. for four days to obtain poly-
40 merized 2-(p-vinylphenyl)nitritotriacetic acid.
The polymer formed stable chelates with cop-
per metal ions.

EXAMPLE 23.

Copolymer of N,N-bis(ar-vinylbenzyl)glycine
and N-(ar-vinylbenzyl)isovaline

- 45 A water solution that was 3.26×10^{-4} M in
respect to N,N-bis(ar-vinylbenzyl)glycine and
 9.28×10^{-4} M in respect to N-(ar-vinylbenzyl)-
isovaline was treated with sodium hydroxide
solution until the pH value was approximately
50 9, and sodium persulphate was added to the
solution to the extent of 0.57 per cent by
weight of the total monomers. The solution
was heated at reflux temperature for 9 hours
to produce a turbid dispersion. The dispersion
55 was acidified to a pH value approximately 2,
and the precipitated copolymer of N,N-bis(ar-
vinylbenzyl)glycine and N-(ar-vinylbenzyl)-
isovaline was collected, washed with acetone,
and dried. The resin formed a strong chelate
60 structure with cupric ions.

EXAMPLE 24.

Copolymer of N-(ar-vinylbenzyl)iminodiacetic
acid and N-(ar-vinylbenzyl)isovaline.

- 65 To a water solution that was 1.86×10^{-3} M
in respect to sodium N-(ar-vinylbenzyl)imino-

diacetate and 4.64×10^{-4} M in respect to N-
(ar-vinylbenzyl)isovaline, sodium salt, at a pH
value of 9, there was added α,α' -azobisiso-
butyronitrile in amount corresponding to 0.51
per cent by weight of the total monomers, and
70 the resulting solution was heated at reflux tem-
perature. After 5 hours, there was added to
the solution sodium persulphate in amount
corresponding to 0.51 per cent by weight of
the total monomers initially charged, and re-
fluxing was continued for 7 hours. The clear,
slightly viscous solution was acidified to a pH
value of approximately 2, and the precipitated
copolymer of N-(ar-vinylbenzyl)iminodiacetic
acid and N-(ar-vinylbenzyl)isovaline was col-
80 lected, washed with acetone, and dried.

EXAMPLE 25.

Copolymer of 2-(p-vinylphenyl)nitritotriacetic
acid and N-(ar-vinylbenzyl)-2-(p-vinyl-
phenyl)glycine.

85 To a water solution that was 8.53×10^{-4} M
in respect to sodium 2-(p-vinylphenyl)nitrito-
triacetate and 1.71×10^{-4} M in respect to N-
(ar-vinylbenzyl)-2-(p-vinylphenyl)glycine,
sodium salt, at a pH value of 9, was added
sodium persulphate in amount corresponding
to 0.67 per cent by weight of the total mono-
mers, and the resulting solution was heated at
reflux temperature. After 7 hours α,α' -azobis-
isobutyronitrile was added to the solution in
95 amount equal to the amount of sodium persul-
fate charged earlier, and refluxing was con-
tinued for 16 hours. The resulting solution
was acidified with HCl to pH 2, and the pre-
cipitated copolymer of 2-(p-vinylphenyl)-
nitritotriacetic acid and N-(ar-vinylbenzyl)-2-
100 (p-vinylphenyl)glycine was collected, washed
with acetone, and dried.

EXAMPLE 26.

Copolymer of N-(ar-vinylbenzyl)iminodiacetic
acid and 2-(p-vinylphenyl)glycine.

105 To a water solution that was 2×10^{-3} M in
respect to sodium N-(ar-vinylbenzyl)iminodi-
acetate and 2×10^{-3} M in respect to 2-(p-
vinylphenyl)glycine, sodium salt, at a pH value
of 9, there was added α,α' -azobisisobutyro-
nitrile in amount corresponding to 0.61 per
cent by weight of the total monomers, and
the resulting solution was heated at reflux tem-
perature for 7 hours. The resulting solution
was acidified with HCl to pH 2, and the pre-
cipitated copolymer of N-(ar-vinylbenzyl)-
iminodiacetic acid and 2-(p-vinylphenyl)-
glycine was collected, washed with acetone,
and dried. The resin product formed a strong
120 chelate structure with cupric ions.

In foregoing Examples 15, 16, 17, 19, 20,
21, 23, 24, 25 and 26, the ar-vinylbenzyl com-
pounds employed as starting materials were
mixtures of isomers consisting essentially of
125 from 60 to 65 per cent by weight of the p-
vinylbenzyl isomer and from 40 to 35 per cent
by weight of the o-vinylbenzyl isomer. In
Examples 4 and 8 the starting material was
substantially the p-vinylphenyl isomer. In 130

place of these particular isomers and mixture of isomers, there can be used any of the individual isomers, i.e., the *o*-vinyl-, the *m*-vinyl-, or the *p*-vinyl isomer, or mixtures of two or more of such isomers, to obtain polymers and interpolymers of the isomeric vinylphenyl aliphatic aminocarboxylic acids.

As noted previously, the vinylphenyl aminocarboxylic acid polymers are solid resinous products which are capable of forming salts of the carboxylic acid group by reaction with ammonia and organic amines, and with metal bases, such as alkali metal and alkaline earth metal bases.

Some of the metal salts, as shown in the foregoing Examples 15 to 26, have chelate structures. In some instances, metal ions form chelates with the free-acid form of the resin. Usually, stable chelates were formed only with the salts of the carboxylic acid group. Many of these chelate salts are stable at neutral to alkaline pH values, but are dissociated at low pH values. Therefore, the amino acid resins can be regenerated from their chelate salt forms by treatment thereof with strong acids such as hydrochloric acid.

For purpose of specific illustration of the use of these chelating resins, the following tests were carried out. An intimate mechanical mixture was prepared comprising two parts by weight of small pieces of polystyrene resin foam and one part by weight of the homopolymeric N-(*ar*-vinylbenzyl)iminodiacetic acid obtained in Example 15. This mixture was placed in a glass tube 15 mm. in diameter and two feet long to provide a fluid-permeable solid resin bed. One hundred milliliters of a 5×10^{-3} M aqueous solution of ferric chloride was slowly passed into the resin bed. Ferric ions were removed from the solution during passage through the bed and were retained by the resin. After rinsing the resin bed with water, the iron-containing resin was regenerated to the acid form by elution with 1N HCl solution, ferric chloride being removed in the effluent.

In another test 0.1085 g. of the homopolymeric N-(*ar*-vinylbenzyl)iminodiacetic acid obtained in Example 15 was dispersed by stirring into 200 ml. of aqueous solution that was 1N in respect to KCl and 1.0155×10^{-3} M in respect to cupric chloride. The resin particles turned blue in color while the aqueous solution became colorless. The resin particles were separated by filtration to yield a filtered solution that was substantially free of copper ions. The copper-containing resin particles were regenerated by washing with 1N HCl solution.

The following additional Examples illustrate the addition interpolymers of the invention but are to be construed as limiting its scope.

EXAMPLE 27.

A solution containing 0.5 g. of N-(*ar*-

vinylbenzyl)iminodiacetic acid, 0.5 g. of sodium *p*-vinylbenzyl-sulphonate, 0.001 g. of sodium persulphate and 100 ml. of water was heated to reflux temperature and re-refluxed for 22 hours. There was thereby obtained a clear, slightly viscous solution which was acidified to a pH value of approximately 1 by addition thereto of hydrochloric acid. The white solid copolymer of N-(*ar*-vinylbenzyl)iminodiacetic acid of *p*-vinylbenzenesulphonic acid was collected, washed and dried. The dried resinous copolymer contained some sodium chloride and had the following analyses:

Nitrogen = 2.80 per cent by weight

Sulfur = 5.52 per cent by weight

The solid resinous copolymer after drying was insoluble in water and aqueous media. The acid form of the resin could be converted to salt forms by reaction with bases such as ammonium bases or metal bases. Chelate structures of the iminodiacetic acid group were formed in the case of salts of metals that have coordinate covalent bonds.

EXAMPLE 28.

A mixture of 92 parts by weight of N-(*ar*-vinylbenzyl)iminodiacetic acid and 8 parts by weight of sodium *ar*, *ar*-divinylbenzenesulphonate was dissolved in about three times its weight of aqueous sodium hydroxide containing enough sodium hydroxide to dissolve the monomers while applying heat to obtain a clear solution. The solution was cooled to room temperature and concentrated hydrochloric acid was added to adjust the pH value of the solution to 8. To this solution was added 0.33 g. of sodium persulphate, and the resulting solution was heated on a steam bath overnight (about 16 hours) to produce a gelled product. After separating most of the water, the gel was washed with acetone and dried. The cross-linked resin product was insoluble in water but was highly swollen in aqueous media. The extent of swelling in aqueous media was least at pH values near the isoelectric point, greater in more acidic media and greatest in strongly alkaline media.

EXAMPLE 29.

In place of the 8 parts by weight of sodium *ar*, *ar*-divinylbenzenesulphonate in Example 28, there was employed 4 parts by weight thereof and 4 parts by weight of N,N-bis(*ar*-vinylbenzyl)iminodiacetic acid, the procedural steps being like those set forth in Example 28. A crosslinked gelled interpolymers of N-(*ar*-vinylbenzyl)iminodiacetic acid, N,N-bis(*ar*-vinylbenzyl)glycine, and *ar*, *ar*-divinylbenzene sulphononic acid was obtained. The properties of this resin product were similar to those of the product obtained in Example 28.

EXAMPLE 30

To a solution of 3.5 g. of N-(*ar*-vinylbenzyl)iminodiacetic acid in 16.5 ml. of

water was added sodium hydroxide until the pH value of the solution was 5.5. A solution of 1.0 g. of acrylamide in water at a pH value of 5.5 was also prepared and added to the solution of N-(ar-vinylbenzyl)iminodiacetic acid. The resulting mixture was heated to 65°C. and deaerated by blowing with nitrogen for one hour. While continuing the nitrogen flow, 0.05 g. of α,α' -azobisisobutyronitrile was added to the solution and the temperature was maintained at 65°C. After 45 minutes the nitrogen flow was stopped. After another hour at 65°C., the temperature was raised to 95°C. for three hours. The resulting gelled product was stirred in 500 ml. of acetone for two hours to obtain a white, crystalline resin which was collected on a filter. The resin was then dispersed in 200 ml. of acetone. After standing in acetone for 16 hours, the resin was collected and dried under vacuum to obtain a substantially quantitative yield of the copolymer of N-(ar-vinylbenzyl) iminodiacetic acid and acrylamide. This resin formed strong chelate structures with cupric and other chelate-forming metal ions.

EXAMPLE 31.

To an alkaline aqueous solution that was $3.26 \times 10^{-3}M$ in respect to N,N-bis(ar-vinylbenzyl)glycine, sodium salt, and $3.26 \times 10^{-3}M$ in respect to sodium acrylate, at a pH value of 10, there was added α,α' -azobisisobutyronitrile in amount corresponding to 0.49 per cent by weight of the combined monomers. After heating at reflux temperature for two hours, the resulting gel was acidified with HCl to a pH value of 2. The precipitated resinous copolymer of N,N-bis(ar-vinylbenzyl)glycine and acrylic acid was collected, washed with 1N HCl and acetone and dried. The resin product formed chelate structures with cupric ions.

EXAMPLE 32.

A solution in benzene $2.62 \times 10^{-3}M$ in respect to diethyl N-(ar-vinylbenzyl) aspartate and $2.32 \times 10^{-3}M$ in respect to vinyl acetate and containing benzoyl peroxide in amount corresponding to 0.5 per cent by weight of the combined monomers was heated at reflux temperature for 3 hours. The benzene was removed by distillation and evaporation under vacuum to obtain a solid resinous copolymer of diethyl N-(ar-vinylbenzyl)aspartate and vinyl acetate. Hydrolysis of the ester linkages with alkali and acidification produced the corresponding resinous copolymer of N-(ar-vinylbenzyl)aspartic acid and vinyl alcohol.

EXAMPLE 33.

To a solution of 60 parts by weight of methanol and 40 parts of water were added 2-(*p*-vinylphenyl)glycine and methyl methacrylate, each in amount corresponding to 1.19×10^{-2} gram-mole per litre, and α,α' -azobisisobutyronitrile in amount correspond-

ing to 1.28 per cent by weight of the combined monomers. After heating at reflux temperature for 4 hours, the resulting solution was concentrated by distillation and evaporation and the residue was diluted with ethanol. The precipitated resinous copolymers of 2-(*p*-vinylphenyl)-glycine and methyl methacrylate was collected and dried.

EXAMPLE 34.

A mixture of 95 parts by weight diethyl N-(ar-vinylbenzyl)aspartate, 5 parts by weight of technical divinylbenzene (approximately 55 per cent by weight divinylbenzene, 35 per cent ethylstyrene and 10 per cent diethylbenzene), and 0.1 part of α,α' -azobisisobutyronitrile was heated on a steam bath for approximately 18 hours to form a solid resinous crosslinked copolymer. The comminuted resin was suspended in 4N H_2SO_4 and heated at refluxed temperature for 16 hours to hydrolyze the ester groups and obtain particles of a solid resinous copolymer of N-(ar-vinylbenzyl)aspartic acid and divinylbenzene.

EXAMPLE 35.

A water solution that was $4.02 \times 10^{-4}M$ in respect to N-(ar-vinylbenzyl)iminodiacetic acid and $1.865 \times 10^{-4}M$ in respect to acrylonitrile and that contained sodium persulphate in amount corresponding to 0.25 per cent by weight of the combined monomers was allowed to stand at 24°C. for 48 hours to produce a water solution of a soluble copolymer of N-(ar-vinylbenzyl)iminodiacetic acid and acrylonitrile.

A starting water solution similar to the one just described but not containing any sodium persulphate or other added catalyst was irradiated with ultraviolet radiation at 24°C. for 48 hours to produce the same result, i.e. formation of a water solution of a soluble copolymer of N-(ar-vinylbenzyl)iminodiacetic acid and acrylonitrile.

A starting solution in dimethyl formamide as a solvent and $1.0 \times 10^{-3}M$ in respect to N-(ar-vinylbenzyl)iminodiacetic acid and $9.43 \times 10^{-2}M$ in respect to acrylonitrile and containing benzoyl peroxide in amount corresponding to 0.25 per cent by weight of the monomers was held at 24°C. for 48 hours to produce a copolymer of N-(ar-vinylbenzyl)iminodiacetic acid and acrylonitrile that was soluble in water.

In the foregoing Examples 27—32 and 34—35, the ar-vinylbenzyl starting material was a mixture of isomers consisting essentially of from 60 to 65 per cent by weight of the *p*-vinylbenzyl compound and from 40 to 35 per cent by weight of the *o*-vinylbenzyl compound. In Example 33, the starting material was essentially the para isomer. In place of the particular isomers or mixtures of isomers employed in these Examples there can be used starting materials corresponding to any of the individual *o*-, *m*-, or

p-vinyl substituted phenyl or benzyl compounds or mixtures or two or more of such isomers to obtain the corresponding polymers of such starting materials.

- 5 As an illustration of such use of these addition interpolmer chelating resins, the following tests were carried out. Particles of the solid, water-insoluble, resinous copolymer of N-(ar-vinylbenzyl)aspartic acid and di-
10 vinylbenzene that was obtained in accordance with the description in Example 34 were placed in an elongated tube to provide a permeable bed of such particles of resin. Into
15 and through the resin bed was passed a stream of aqueous solution having the following composition and a pH value of 4.5.

KCl	1M
Acetic Acid	0.1M
Potassium Acetate	0.1M
CuCl ₂	0.1M

- 20 The effluent salt solution was free of cupric ions. The metal-containing resin was regenerated by passing aqueous hydrochloric acid through the resin bed, cupric chloride being
25 removed in the effluent.

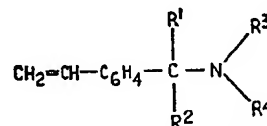
- Instead of passing an aqueous cupric ion solution into the resin bed, aqueous solutions containing (in successive separate tests) ions of cobalt (II), nickel (II), and iron (III),
30 respectively, were passed into the regenerated resin bed. In each instance, the metal ion was retained by the resin in chelated structure, and the aqueous effluent was devoid of that metal ion. In each instance the metal-
35 containing resin was regenerated with strong hydrochloric acid.

- By way of specific illustration of the use of these chelating resins, particles of poly-
40 meric N-(ar-vinylbenzyl)iminodiacetic acid were placed in a vertical tube and a dilute solution of cupric chloride was passed through the resin bed. The effluent was free of cupric ions until the resin bed was converted to the copper chelate form. The ex-
45 hausted resin was readily regenerated by elution with strong acid, e.g. hydrochloric

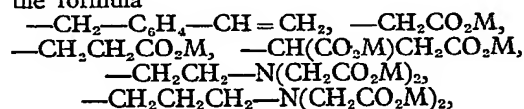
acid. In such a cycle, the capacity of the polymeric α -aminocarboxylic acid resin bed was 3.7 millimoles of cupric ion per gram of the resin. In similar manner, the resin can
50 remove from solutions passed therethrough ions of cobalt, iron, nickel, mercury, calcium and like chelate-forming metals.

WHAT WE CLAIM IS:—

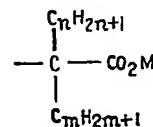
1. Polymerizable vinylphenyl aminocarboxylic compounds having the general
55 formula:—



wherein R¹ represents a hydrogen atom or a radical having the formula —CO₂M or
60 —CH₂CO₂M, R² represents a hydrogen atom or a methyl group, R³ and R⁴ are the same or different and each represent a hydrogen atom, a methyl group or a radical having
65 the formula

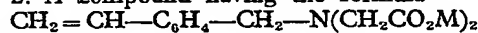


or



where M is a hydrogen atom, an ammonium radical or a metal, *n* is an integer from 1 to 4 inclusive and *m* is 0, 1 or 2, and wherein at
75 least one of the radicals represented by R¹, R³ and R⁴ contains a carboxyl group, and solid resinous polymers and resinous addition interpolymers of said polymerizable
80 vinylphenyl aminocarboxylic compounds.

2. A compound having the formula



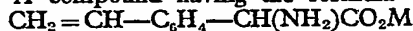
where M is as defined in claim 1.

3. A compound having the formula



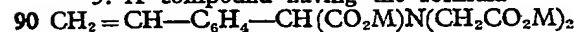
- 85 where M is as defined in claim 1.

4. A compound having the formula



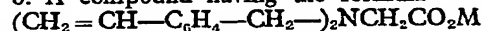
where M is as defined in claim 1.

5. A compound having the formula



where M is as defined in claim 1.

6. A compound having the formula



where M is as defined in claim 1.

- 95 7. A solid resinous homopolymer of one polymerizable vinylphenyl aminocarboxylic compound as claimed in any of claims 2 to 6.

8. A solid resinous copolymer of at least two polymerizable vinylphenyl aminocarboxylic compounds as claimed in any of

claims 2 to 6, as the only polymerically combined ingredients.

9. A resinous addition interpolmer containing, in polymerically combined form, an appreciable proportion of (A) at least one
105 vinylphenyl aminocarboxylic compound as claimed in claim 1 and (B) at least one polymerizable ethylenically unsaturated compound that is different from the compounds of (A).
110

10. A resinous addition interpolmer according to claim 9, wherein there are polymerically combined from 1 to 99 parts by weight of (A) and from 99 to 1 parts by
115 weight of (B).

11. A resinous addition interpolmer

according to claim 9 or 10, wherein (B) is an alkenylaromatic compound.

12. A resinous addition interpolymer according to claim 9 or 10, wherein (B) is a divinylbenzene.

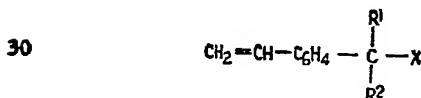
13. A resinous addition interpolymer according to claim 9 or 10, wherein (B) is acrylic acid, methacrylic acid or a derivative thereof.

14. A resinous addition interpolymer according to claim 9 or 10, wherein (A) is an N-(ar-vinylbenzyl)iminodiacetic acid or derivative thereof, or an N-(ar-vinylbenzyl)-aspartic acid or a derivative thereof.

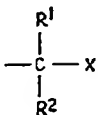
15. A resinous addition interpolymer according to claim 9, containing, in polymerically combined form, at least 50 per cent by weight of an N-(ar-vinylbenzyl)iminodiacetic acid or a derivative thereof.

16. A resinous addition interpolymer according to claim 9, containing, in polymerically combined form, at least 50 per cent by weight of an N-(ar-vinylbenzyl) aspartic acid or a derivative thereof.

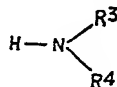
17. A process for the preparation of a vinylphenyl aminocarboxylic compound or a polymer thereof according to claim 1, which comprises reacting a compound of the general formula:



- wherein R¹ represents a hydrogen atom or a radical having the formula —CO₂M, or —CH₂CO₂M, where M is as previously defined, R² represents a hydrogen atom or a methyl group and X represents a halogen atom or an amino radical having at least one amino hydrogen atom, or the whole group

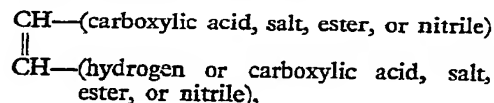


- represents the formyl group, with (a) an aminocarboxylic acid, salt, ester, or nitrile having an >NH or —NH₂ group when X is a halogen atom, said aminocarboxylic reactant having the general formula

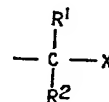


- wherein R³ and R⁴ correspond to the radicals previously defined and at least one of R³ and R⁴ contains a carboxylic acid, salt, ester, or nitrile group, (b) an ethylenically unsaturated carboxylic acid, salt, ester, or nitrile or a halo-

carboxylic acid when X is an amino radical having at least one amino hydrogen atom, said ethylenically unsaturated carboxylic or nitrile reactant having the general formula



or (c) an alkali cyanide and ammonia when



is the formyl group, and hydrolyzing the reaction product where necessary, to obtain said vinylphenyl aminocarboxylic compound, which may then be polymerized under free radical-inducing conditions.

18. A process according to claim 17, in which an aliphatic aminocarboxylic acid, salt, ester or nitrile wherein the amino group has at least one hydrogen atom and is in one of the positions α- or β- relative to the carboxylic group is reacted with an ar-vinylbenzyl halide in the presence of aqueous alkali to form a vinylphenyl aminocarboxylic compound having the formula set forth in claim 1, which may then be polymerized under free radical-inducing conditions.

19. A process according to claim 18, in which iminodiacetic acid is reacted with an ar-vinylbenzyl chloride to produce an N-(ar-vinylbenzyl)imino-diacetic acid.

20. A process according to claim 18, in which an ar-vinylbenzyl chloride is reacted with glycine to produce an N,N-[bis(ar-vinylbenzyl)]glycine.

21. A process according to claim 17, in which an ar-vinylbenzylamino compound having at least one amino hydrogen atom is reacted with diethyl maleate or acrylonitrile and the resulting reaction product is hydrolyzed to form a vinylphenyl aminocarboxylic compound having the formula set forth in claim 1, which may then be polymerized under free radical-inducing conditions.

22. A process according to claim 21, in which diethyl maleate is reacted with an ar-vinylbenzyl amine and the resulting reaction product is hydrolyzed to produce an N-(ar-vinylbenzyl) aspartic acid.

23. A process according to claim 17, in which a monohaloacetic acid is reacted with an ar-vinylbenzylamino compound having at least one amino hydrogen atom in the presence of aqueous alkali to form a vinylphenyl aminocarboxylic compound having the formula set forth in claim 1, which may then be polymerized under free radical-inducing conditions.

18. A process according to claim 16 or 17,

24. A process according to claim 17, in which a 2-(ar-vinylphenyl)glycine is reacted with at least two molecular proportions of an alkali chloroacetate in an alkaline aqueous reaction mixture to produce a 2-(ar-vinylphenyl)-nitrilio-triacetic acid. 15
- 5 25. A process according to claim 17, in which an ar-vinylbenzaldehyde is reacted with an alkali cyanide and ammonia in an alkaline aqueous reaction mixture to form a 2-(ar-vinylphenyl)-glycine, which may then be polymerized under free radical-inducing conditions. 20
- 10 26. A method of making a solid resinous polymer according to claim 7 or 8, which comprises subjecting at least one polymerizable vinylphenyl aminocarboxylic compound having the formula set forth in claim 1 to free radical-inducing conditions.
27. A method according to claim 26, wherein a single polymerizable vinylphenyl aminocarboxylic compound is subjected to free radical-inducing conditions to obtain a homopolymer of such vinylphenyl aminocarboxylic compound.
- STEVENS, LANGNER, PARRY &
ROLLINSON,
Chartered Patent Agents,
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1961.
Published by The Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies may be obtained.

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